Critical Fields and Hysteresis Effects in Tin Films

J. P. BALDWIN

Mullard Research Laboratories, Redhill, Surrey, England

INTRODUCTION

Recent measurements of the critical fields in thin films[1-3] indicate that the nonlinear theory of Ginzburg and Landau[4] (GL) does not fully account for superconductivity in thin films. Liniger and Odeh[5] have applied a nonlocal modification of the GL theory to the case of thin films assuming boundary conditions corresponding to diffuse scattering of electrons at the film surfaces. We wish to discuss our measurements of critical fields and hysteresis in magnetic field phase transitions in tin films by referring to the results of this theory.

THEORETICAL DISCUSSION

Bardeen[6] changed the nonlinear GL equations to a nonlocal form by modifying part of the kinetic energy term in the GL free energy expression. On integrating the free energy over the film thickness and minimizing with respect to the normalized order parameter ϕ, and on putting in the kernel function of the Pippard theory,[7] Eq. (2.35) of the paper by Liniger and Odeh can be obtained, namely,

$$(D/\xi_0)(1-\phi^2) = \tfrac{3}{8}\,(\xi_0/\delta_0)^2(H/H_{CB})^2 Y(\phi,D,\delta_0,\xi_0)\,, \tag{1}$$

where D is the film thickness, ξ_0 is the coherence length, δ_0 is the penetration depth at zero field, H is the magnetic field applied parallel to the film surfaces, H_{CB} is the critical field of the bulk material, and ϕ is the ratio of the order parameter in the thin film to the order parameter at zero field. ϕ is assumed to be constant over the film thickness.

The function Y in Eq. (1) is a double integral over the film thickness involving the Pippard kernel function and a normalized vector potential as a function of distance from the center of the film obtained by solving the nonlocalized GL equation.

The critical value of H, H_{CF}, for the phase change in thermodynamic equilibrium is obtained by combining Eq. (1) with the condition that the Gibbs free energies in the superconducting and normal phases are equal. However, if one puts ϕ equal to zero, Eq. (1) alone is sufficient to determine the critical field at the second-order phase transition. Liniger and Odeh therefore express Y as

$$Y = Y_0 + \phi^2 Y_1\,, \tag{2}$$

which will always be accurate at, and close to, the second-order phase change.

Combining Eqs. (1) and (2) we find that

$$\phi^2 = \frac{1-\frac{3}{8}\,(\xi_0^3/D\delta_0^2)(H_{CF}/H_{CB})^2 Y_0}{1+\frac{3}{8}\,(\xi_0^3/D\delta_0^2)(H_{CF}/H_{CB})^2 Y_1}\,. \tag{3}$$

ϕ is zero at a second-order phase change, therefore putting the numerator of Eq. (3) equal to zero gives the thin film critical field at such a phase change in the form

$$H_{CF}/H_{CB} = (2\sqrt{2}/\sqrt{3})(\delta_0/D)(D^3/\xi_0^3 Y_0)^{\frac{1}{2}}. \tag{4}$$

ϕ, which must be real, can differ from zero when the denominator of Eq. (3) becomes negative, in which case the phase transitions become first order and involve a latent heat. Under these circumstances hysteresis can be observed in the phase transitions due to supercooling and superheating effects. The point where second-order phase transitions change over to first order, i.e., where the hysteresis effects will begin to occur, can be obtained from Eq. (3) by putting the numerator and denominator both equal to zero. This gives the condition

$$Y_0 = -Y_1\,. \tag{5}$$

Combining Eqs. (4) and (5) and using the notation $Y_1/(D/\xi_0)^3 = (D/\delta_0)^2\theta(D/\xi_0)$ [Eq. (2.45) of the paper by Liniger and Odeh], we find a critical value $(H_{CF}/H_{CB})_C$, where

$$(H_{CF}/H_{CB})_C = (2\sqrt{2}/\sqrt{3})(D/\xi_0)^3[-\theta(D/\xi_0)]^{\frac{1}{2}}/Y_0\,. \tag{6}$$

For thick films, so far as the approximation ϕ = constant thicknesswise is valid, using the limits $Y_0 = (D/\xi_0)^3/9$ and $\theta = -1/45$ as $D\to\infty$ given by Liniger and Odeh, the condition (6) gives the same result as the GL theory, namely,

[1] R. H. Blumberg, J. Appl. Phys. **33**, 182 (1962).
[2] A. M. Toxen, Phys. Rev. **127**, 382 (1962).
[3] D. H. Douglass, Jr., and R. H. Blumberg, Phys. Rev. **127**, 2038 (1962).
[4] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor Fiz. **20**, 1064 (1950).
[5] W. Liniger and F. Odeh, IBM Research Paper R.C.–858, 1962 (unpublished).
[6] J. Bardeen, in *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. XV, Sec. 11, p. 274.
[7] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

$$(H_{CF}/H_{CB})_C = 2.19 \,. \qquad (7)$$

For very thin films relative to ξ_0, Liniger and Odeh show that $Y_0 \to (D/\xi_0)^4/16$, and our numerical calculations indicate that $\theta \to -0.00756\ (D/\xi_0)^2$. Thus, condition (6) gives

$$(H_{CF}/H_{CB})_C \simeq 2.27 \qquad (8)$$

in this case.

Comparing Eqs. (7) and (8) we see that the measurable quantity $(H_{CF}/H_{CB})_C$ at the change over from first- to second-order phase transitions is a very weak function of the film thickness relative to ξ_0, and does not differ greatly from the value given in the GL theory.

CRITICAL FIELD MEASUREMENTS

For the critical field and hysteresis measurements, tin film specimens were evaporated on to glass sub-

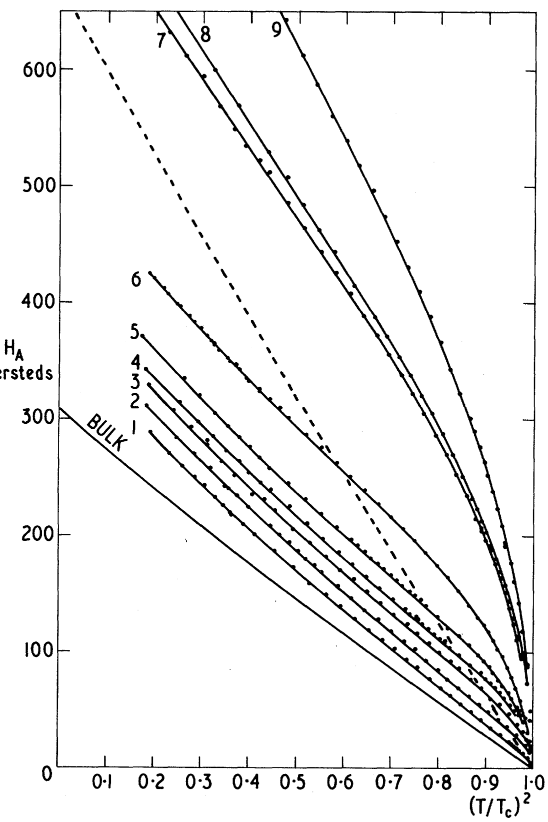

Fig. 1. Graphs of critical field versus $(T/T_c)^2$ for tin films 1 to 9, having thicknesses 6450, 4650, 3500, 2730, 2460, 2070, 1240, 1200, and 1090 Å, respectively.

strates at about 20°C in vacua better than 2×10^{-6} Torr during deposition. Specimen profiles were outlined by cutting the films with razor blades, and the specimens were accurately aligned with the field produced by a solenoid calibrated by NMR techniques. The effect of the earth's field was eliminated using Helmholtz coils.

Increasing-field critical fields, H_A, of 9 tin films are presented as a function of the square of the reduced temperature, in Fig. 1. The results agree well with those of Blumberg[1] for very thin tin films deposited on substrates cooled with liquid nitrogen.

The variation of H_A with film thickness is shown on log scales in Fig. 2 for the temperatures

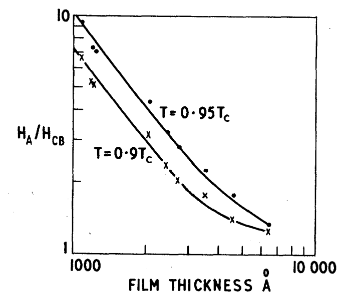

Fig. 2. Tin film critical fields as a function of film thickness at two temperatures.

$T = 0.95T_c$ and $T = 0.9T_c$, where T_c is the film critical temperature. Identifying H_A as H_{CF}, Fig. 2 shows that, for the thinner films where the phase transition is second order, H_A varies at least as the inverse 1.25 power of the film thickness in contradiction to the inverse 1.0 power predicted by the GL theory (cf. Toxen[2]).

The graph at 0.95 T_c in Fig. 2 coincides quite well with that predicted by Liniger and Odeh using Eq. (4) with $\delta_0 = 1000$ Å and $\xi_0 = 2000$ Å. This value of coherence length is about the value for tin[8] so that the results suggest a value $\delta_0 = 1000$ Å at $T = 0.95\ T_c$ for tin. If this result is extrapolated to zero temperature using the Bardeen–Cooper–Schrieffer[8] (BCS) relation for the temperature variation of penetration depth, a value 390 Å is obtained for the zero-temperature London penetration depth. Using the factor 1.6 given by BCS for random scattering to convert to the penetration depth at zero temperature, a value 620 Å is obtained. This compares with the value 510 Å obtained by Faber and Pippard[9] and so is rather high.

HYSTERESIS MEASUREMENTS

The available evidence suggests that superheating does not occur in our phase transitions, so that we may identify the increasing-field critical fields with H_{CF}. The observed hysteresis due to supercooling is

[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[9] T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955).

$H_A - H_B$, where H_B is the decreasing-field critical field.

The dotted line in Fig. 1 is the locus of points where the ratio $H_{CF}/H_{CB} = 2.19$. Hysteresis measurements on specimens 1 to 6 showed that no hysteresis was observed in the phase transitions at temperatures higher than indicated by this dotted line. In every case the hysteresis began to be observable at temperatures just lower than those indicated by the dotted line, and thereafter the hysteresis increased with decreasing temperature.

In a previous paper[10] we calculated the maximum possible supercooling which would give the maximum possible hysteresis, $H_A - H_{C1}$, in the magnetic field phase transitions, using the GL theory. The graph of $(H_A - H_{C1})/H_{CB}$ versus H_A/H_{CB} is shown in Fig. 3. At values of H_A/H_{CB} close to 1.0 this graph is dotted because the approximation that the order parameter is constant over the film thickness is not valid here.

For values of H_A/H_{CB} close to 2.19, it will clearly be difficult to detect hysteresis because it is tending smoothly to zero. Thus the best we can do to test that the hysteresis tends to zero at or close to $H_A/H_{CB} = 2.19$ is to compare experimental graphs of $(H_A - H_B)/H_{CB}$ versus H_A/H_{CB} with Fig. 3. The experimental graphs for five films are drawn in Fig. 4, and show that the hysteresis always tends to zero at values of H_A/H_{CB} close to about 2.19 or rather less in the case of the thinnest film (film 6). We may therefore say that the hysteresis measurements support the theoretical result that the ratio H_A/H_{CB} at the change over from first-order to second-order phase transitions is close to the value given by the GL theory, and is a very weak function of film thickness at least down to thicknesses of the order of the coherence length.

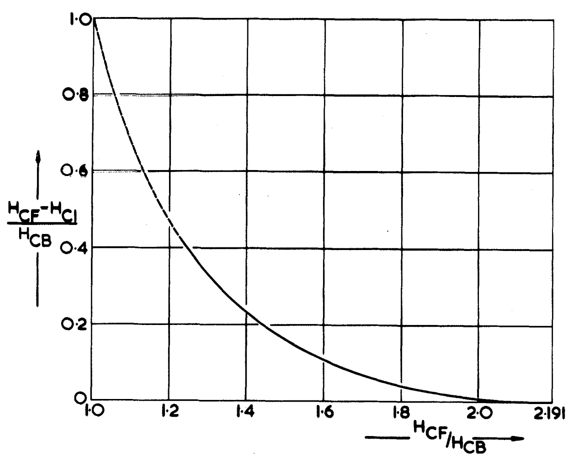

FIG. 3. The graph of $(H_{CF} - H_{C1})/H_{CB}$ versus H_{CF}/H_{CB} calculated from the Ginzburg–Landau theory for $K = 0$.

By comparing the ordinates of Fig. 4 with those in Fig. 3 we see that typically only about $\frac{1}{6}$ of the theoretical maximum hysteresis is observed presumably due to the existence and spreading of superconducting nuclei in the otherwise normal film. It was rarely possible to observe abrupt resistance changes in the supercooled transitions due to propagation of the superconducting phase over a significant length of the film strips. However, such propagation effects were consistently observed for the case of one particular film.

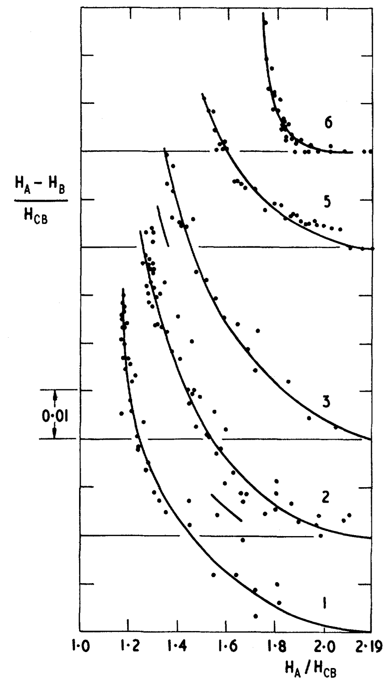

FIG. 4. The experimental measurements of $(H_A - H_B)/H_{CB}$ versus H_{CF}/H_{CB} to compare with Fig. 3.

CONCLUSION

The nonlocal nonlinear theory of Liniger and Odeh is in general agreement with our measurements of critical fields and hysteresis effects in tin films.

ACKNOWLEDGMENTS

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[10] J. P. Baldwin, Phys. Letters **3**, 223 (1963).

Discussion 52

LYNTON: I didn't quite catch the dependence on thickness that you said the Ginzburg–Landau theory predicted.

J. P. BALDWIN *Mullard Research Laboratories:* An inverse thickness.

LYNTON: According to the equation you had on the board it goes as λ_0/d, where λ_0 is the experimental penetration depth which is never implied to be a constant in the Ginzburg–Landau theory.

BALDWIN: Yes, quite. So that lambda is in fact related to the thickness.

MEISSNER: I would like to remind you that about eight years ago Maxwell and Lutes made quite similar hysteresis observations on tin whiskers. [O. S. Lutes and E. Maxwell, Phys. Rev. **97**, 1718 (1955); O. S. Lutes, *ibid.* **105**, 1451 (1957)].

Superconductivity of Thin Films of Niobium

H. LONDON and G. R. CLARKE
Atomic Energy Research Establishment, Harwell, England

The object of this investigation is to determine the critical currents in niobium films as a function of temperature and magnetic field and to study the critical phenomena in detail.

The method is similar to that used by Mercereau and Crane[1] in their study of tin films. Supercurrents are induced in a cylindrical film by a primary coil and measured by a secondary coil. But whereas Mercereau's films have the shape of a short ring, our films are long cylinders surrounded by short coils. This geometry was chosen in order to avoid field concentration at the edges of the film. A screen of high-purity aluminium was necessary for the suppression of the low frequency ripple from a liquid-nitrogen-cooled solenoid which surrounds the cryostat. This solenoid can produce fields up to 15000 Oe. The primary coil is supplied with alternating current of either 18 to 100 cps or 0.05 to 0.3 cps. The voltage picked up by the secondary is integrated either electronically or in a galvanometer–photocell arrangement. This enables one to display the instantaneous flux through the secondary as the y deflection on an oscilloscope. The x deflection is connected to a current shunt in the primary circuit.

The films are produced by evaporation from an electrically heated niobium wire of 1-mm diameter which has the shape of a twisted hairpin and is positioned at the axis of a glass tube of 42-mm i.d. The deposition rate is 0.3 Å/sec and the vacuum of the order of 10^{-10} mm Hg. This corresponds to a purity of the film of 0.1 to 1 at. %. The substrate temperature during the deposition is about $-100°$ C. The film remains under vacuum throughout the measurements. The thickness of the film can be estimated from the increase of the resistance of the niobium wire and can later be determined by quantitative analysis. The normal resistance of the film is monitored by a single layer coil connected to a Q meter. This gives its first response about 20 sec after the start of the deposition indicating that the film becomes coherent when its nominal thickness is about 6 Å. This coil can also be used as an alternative to the usual coil system for measuring critical currents and temperatures on the freshly deposited film before it has been exposed to room temperature. One film was later subjected to further heat treatment.

The properties of two films of different thickness are listed in Table I. The normal resistivity is given in arbitrary units which are different for the two films. The critical currents are expressed in terms of H_{Ic}, the difference of the magnetic field which the critical current produces on the two sides of the film. The values of the critical magnetic field H_u at 4.2°K are obtained by extrapolation from a nearly linear H_u versus T plot obtained at higher temperatures.

For the discussion of the details of the critical current loops we first consider the idealized case of a coil system that is long in relation to its diameter. The radius of the film is R_F and the radius of the secondary is R_s, the field produced by the primary is H_p and the currents in the film are expressed by the magnetic field difference H_I which they produce. The flux Φ through the secondary is expressed in terms of $\phi = \Phi/\pi R_F^2$. It is plotted on the oscillograms as a function of H_p. The normal resistance of the film is so high that at the frequencies used the induced currents are unobservable. Thus in the normal state the ϕ vs H_p curve is a straight line of slope R_s^2/R_F^2. If the film is superconductive, the slope will be $(R_s^2 - R_F^2)/R_F^2$.

[1] J. E. Mercereau and L. T. Crane, Phys. Rev. Letters **9**, 381 (1962).